# Charged defects-controlled conductivity in Ge-In-Se glasses

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**The variation of the d.c. electrical conductivity, a, with composition and temperature was investigated for glasses of the Ge-In-Se system. The results indicate a decrease in the activation energy for electrical conductivity, $\Delta E$, and an increase in $a$ on introduction of indium into Ge-Se glasses. The changes in $\Delta E$ and $a$ with composition (selenium content in the glasses) are identical for the $Ge_x In_n Se_{95-x}$ and $Ge_x In_8 Se_{92-x}$ families. The results have been traced to the conduction controlled by charged defects in these chalcogenide glasses. The changes in $\Delta E$ and a have been explained by a shift in the Fermi level, being brought by the introduction of indium.**

## 1. Introduction

Glass formation in the Ge-In-Se system occurs up to about 15 at % In, 60-90 at % Se, the rest being germanium [1]. Data on the density and the glass transition temperature, $T_g$, of several glass compositions of this system have been published recently [2, 3]. Except for a study [4] on the effect of indium as a "dopant" in affecting the activation energy for electrical conductivity, $\Delta E$, in the $Ge_{20}Se_{80}$ glass, the electrical properties of this system have received little attention.

In order to investigate features corresponding to the various topological and chemical effects, the necessity of studying property variation across specific families of various chalcogenide glass systems has already been pointed out [2, 3, 5]. Therefore, the dependences of the mean atomic volume and $T_g$ on the average coordination number, Z, were studied by choosing compositions of families with 5 and 8 at % In in the Ge-In-Se system. The range of Z in the family with 5 at % In was extended [2, 3] by considering neighbouring compositions from families with 3 and 4 at % In.

Characterization of these glasses was continued by studying the variation of the d.c. electrical conductivity, a, from room temperature up to the respective glass transition temperature. As in earlier studies [2, 3], the compositions belonged to the $Ge_xIn_5Se_{95-x}$ and $Ge_xIn_8Se_{92}$ families and also those along the $GeSe_2$-$In_2Se_3$ tie line.

## 2. Experimental procedure

The glasses were prepared by the standard melt-quenching method. Typically, 6 g total (per batch) of appropriate quantities of 99.999 % pure germanium, indium and selenium (procured from Atomergic Chemmetals Corporation, USA) were weighed into cleaned fused silica ampoules ( 12 mm diameter). The ampoules were evacuated to $10^{-5}$ torr (1 torr = 133.322 Pa) and sealed under this vacuum. The preparation was carried out at a temperature of 800 °C for about 10 h, at the end of which the ampoules were quenched in iced water to obtain the glasses. During preparation, the ampoules were continuously rotated to ensure complete mixing of the various constituents. Only compositions which were glassy, as inferred from their X-ray powder diffractograms, were considered for the measurements.

As in the earlier studies [6, 7], the samples for a measurements were flat (typically 1 mm thick) with opposite surfaces rendered parallel. The contacts to the samples were through silver paste electrodes (typically 5 mm diameter). A voltage of 5 V d.c. was applied to the samples and the current measured using a Keithley model 610C electrometer. A chromel-alumel thermocouple, situated very close to the sample, registered the temperature.

Measurements were made on as-quenched samples and also on samples annealed by holding them for 15 min at the respective $T_g$, and then cooling slowly. For any specified composition, measurements were made on multiple samples (two to four) from parallel batch preparations to assess the scatter in the $\Delta E$ and a values.

## 3. Results

The variation of log a with 1/T of the various glass compositions is depicted in Figs 1-4, from which a dependence of the type $a = C \exp(-\Delta E/2kT)$, where C is constant, with a single $\Delta E$ is seen over most of the temperature range investigated. For a few compositions, the slope of the log a versus 1/T data decreased at temperatures between 300 and 350 K. Annealing was found to increase $\Delta E$ by 0.1-0.15 eV for the various compositions; the magnitude of a was found to decrease on annealing by 0.2-0.4 in log units, depending on the temperature and composition. Only data on annealed samples are reported (Table I) and discussed here.

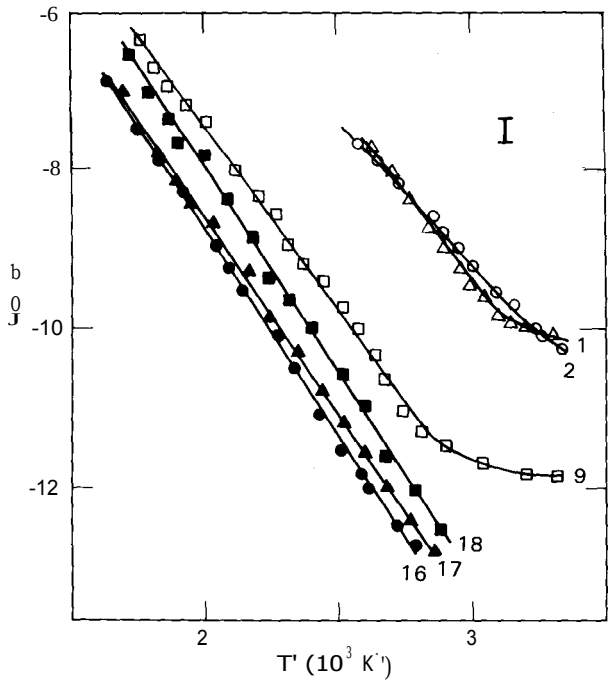


*Figure 1* Variation of log cr with I/T for the Ge-In-Se glasses. The numbers refer to the composition numbers listed in Table I.

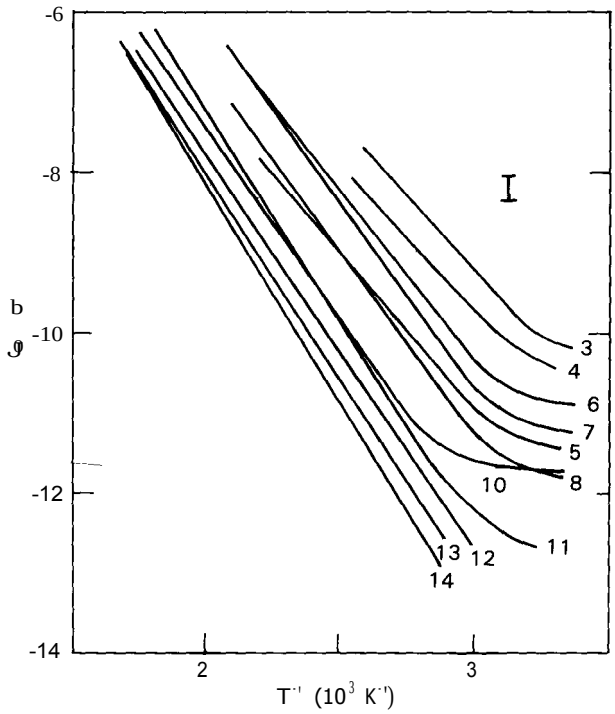


*Figure 2* Loge versus 1/T data for the $Ge_sIn_5Se_{95\ s}$ glasses. To avoid confusion due to overcrowding of data points, only the continuous lines drawn through the data points are shown for these compositions.

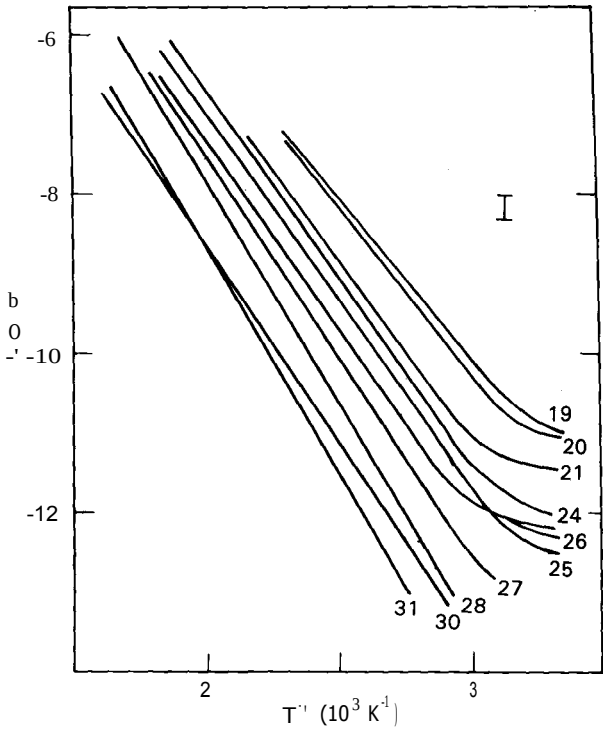


*Figure 3* Log $e$ versus I/ T data for the Ge.1nsSe92 = glasses. To avoid confusion due to overcrowding of data points, only the continuous lines drawn through the data points are shown for these compositions.

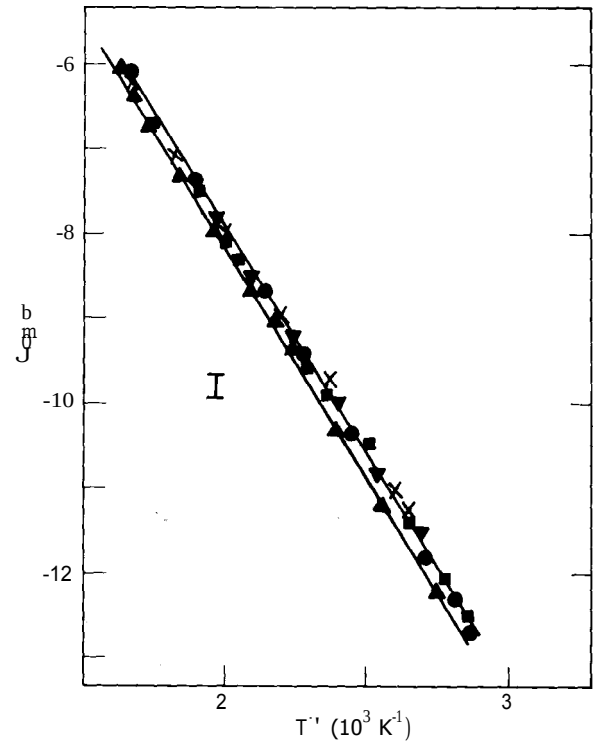


*Figure 4* Variation of log $e$ with 1/T for the tie-line compositions of the system with (A) 5, (•) 8, (0) 10, ( x )12 and (V) 15 at % In.

A temperature of 360 K was chosen at which to study the composition dependence of a of the various glasses, and the *AE* and e data are depicted in Fig. 5a and b. The variation of *AE* and a is the same for the glasses of the two families investigated. *AE* is essentially constant (at around 1.05 eV) for selenium contents of up to 69 at %, after which a decrease of *AE* with increasing selenium content is seen for the glasses of the two families. The factor C can be taken to be essentially constant at $3 \times 10^2$ 52-1 $CM^{-t}$ for the various compositions of the two families of the system (Table I).

The data of Fig. 4 indicate that *AE*, log a and therefore log C are all invariant (within experimental error) across the $GeSe_2$-$In_2Se_3$ tie-line compositions.

TABLE -I Data on $T_g$, AE, loga and logC for the Ge-In-Se glasses

| No. | Ge | In | Se | T, (K) [3] | AE (eV) | - Log 6 (at 360 K) | Log C |
|---|---|---|---|---|---|---|---|
| 1. | 11 | 3 | 86 | 365 | 0.79 | 8.47 | 2.60 |
| 2. | 11 | 4 | 85 | 367 | 0.75 | 8.40 | 2.10 |
| 3. | 12 | 5 | 83 | 372 | 0.77 | 8.37 | 2.42 |
| 4. | 13 | 5 | 82 | 378 | 0.76 | 8.90 | 1.75 |
| 5. | 16 | 5 | 79 | 419 | 0.82 | 9.90 | 1.50 |
| 6. | 18 | 5 | 77 | 442 | 0.86 | 9.40 | 2.66 |
| 7. | 20 | 5 | 75 | 472 | 0.90 | 9.66 | 2.95 |
| 8. | 22 | 5 | 73 | 495 | 0.94 | 10.26 | 2.92 |
| 9. | 25 | 5 | 70 | 550 | 0.96 | 11.10 | 2.36 |
| 10. | 26 | 5 | 69 | 557 | 1.01 | 11.10 | 3.06 |
| 11. | 26.50 | 5 | 68.50 | 564 | 1.05 | 11.30 | 3.42 |
| 12. | 27 | 5 | 68 | 575 | 1.02 | 11.60 | 2.69 |
| 13. | 28 | 5 | 67 | 601 | 1.01 | 12.00 | 2.16 |
| 14' | 29.17 | 5 | 65.83 | 624 | 1.14 | 12.30 | 3.73 |
| 15. | 29.50 | 5 | 68.50 | 622 | 1.06 | 12.30 | 2.56 |
| 16. | 30 | 5 | 65 | 622 | 1.04 | 12.80 | 1.80 |
| 17. | 32 | 5 | 63 | 601 | 1.00 | 12.50 | 1.51 |
| 18. | 35 | 5 | 60 | 567 | 1.02 | 12.00 | 2.30 |
| 19. | 14 | 8 | 78 | 409 | 0.82 | 9.20 | 2.30 |
| 20. | 16.50 | 8 | 75.50 | 436 | 0.84 | 9.35 | 2.43 |
| 21. | 19 | 8 | 73 | 481 | 0.91 | 10.10 | 2.66 |
| 22. | 20.50 | 8 | 71.50 | 502 | 0.91 | 10.10 | 2.66 |
| 23. | 21.50 | 8 | 70.50 | 516 | 0.91 | 10.10 | 2.66 |
| 24. | 22.50 | 8 | 69.50 | 530 | 0.94 | 10.40 | 2.78 |
| 25. | 23.50 | 8 | 68.50 | 549 | 0.96 | 10.66 | 2.80 |
| 26. | 24.50 | 8 | 67.50 | 559 | 0.98 | 11.03 | 2.71 |
| 27. | 25.50 | 8 | 66.50 | 591 | 1.01 | 11.50 | 2.66 |
| 28.' | 26.67 | 8 | 65.33 | 614 | 1.15 | 12.25 | 3.77 |
| 29. | 27.50 | 8 | 64.50 | 610 | 1.05 | 12.60 | 2.12 |
| 30. | 28 | 8 | 64 | 602 | 1.05 | 12.50 | 2.22 |
| 31. | 30 | 8 | 62 | 580 | 1.14 | 13.20 | 2.78 |
| 32.' | 25 | 10 | 65 | 606 | 1.15 | 12.25 | 3.77 |
| 33' | 23.33 | 12 | 64.67 | 600 | 1.15 | 12.25 | 3.77 |
| 34.' | 20.83 | 15 | 64.17 | 593 | 1.15 | 12.25 | 3.77 |

'Tie-line compositions.

## 4. Discussion

### 4.1. Composition dependence of *AE* and *6*

Comparison of the c and $AE$ data obtained here for the Ge-In-Se glasses with those of the Ge-Se glasses [8] is possible by treating indium as an additive or modifier, similar to that in an earlier work [4] for the $Ge_{20}Se_{80}$ glass. It would be more appropriate to vary the indium content in such a study; however, as already mentioned in Section 1 and discussed in detail elsewhere [2, 3, 5], studies on specific families of the Ge-In-Se system were undertaken mainly to infer features due to topological and chemical-ordering effects. Results on $AE$ and o of the same compositions are qualitatively rationalized here based on the c data of similar materials [4, 9, 10].

Although no regular dependence of $AE$ and log 6 with Ge/Se content is seen for the Ge-Se glasses [8], the narrow range of the variation of these parameters across the various compositions enables one to arrive at a value of 1.07 eV for $AE$, - 11.75 $Q^{-1}cm^{-1}$ for log a (at 360 K), giving a value of 3.25 for log C of these glasses. A comparison of the corresponding glasses of the Ge-Se and Ge-In-Se systems indicates that addition of indium results in an increase of 6 of up to 3.3 orders of magnitude; the factor C has correspondingly decreased from 2 x $10^3$ S2-t $cm^{-1}$ to 3 x 102 $Q\text{-}1\ cm\text{-}t$ on introduction of indium. Further, the values of C in the range of 102-103 $D\text{-}1\ cm\text{-}t$ for the Ge-Se and the Ge-In-Se glasses indicate [11] that the conductivity is due to carriers in the extended states below the valence band (considering the p-type conductivity of these glasses). The increase in a on introduction of indium into Ge-Se glasses is, therefore, due to neither changes in C nor in mobility, but is due to a decrease in the activation energy. For the Ge-In-Se glasses with selenium content higher than 80 at %, a reduction of $AE$ by 0.3 eV is seen on addition of indium. The magnitude of this decrease decreases with decreasing selenium content; glasses with selenium content less than ~-_ 69 at % do not register changes in $AE$ on introduction of indium into Ge-Se glasses.

The reduction of $AE$ on addition of indium to Ge-Se glasses indicates a shift of the Fermi level [4]; considering the normal p-type conductivity of chalcogenide glasses, the shift of the Fermi level is towards the valence band.

In amorphous semiconductors, the localized defect states in the gap are known to form various discrete energy levels [12, 13]. Further, in these materials there is a spectrum of charged defect electronic configurations created by the localized defect states in the gap; it is sufficient for the purposes of this paper to realize that there are two major types of defect electronic

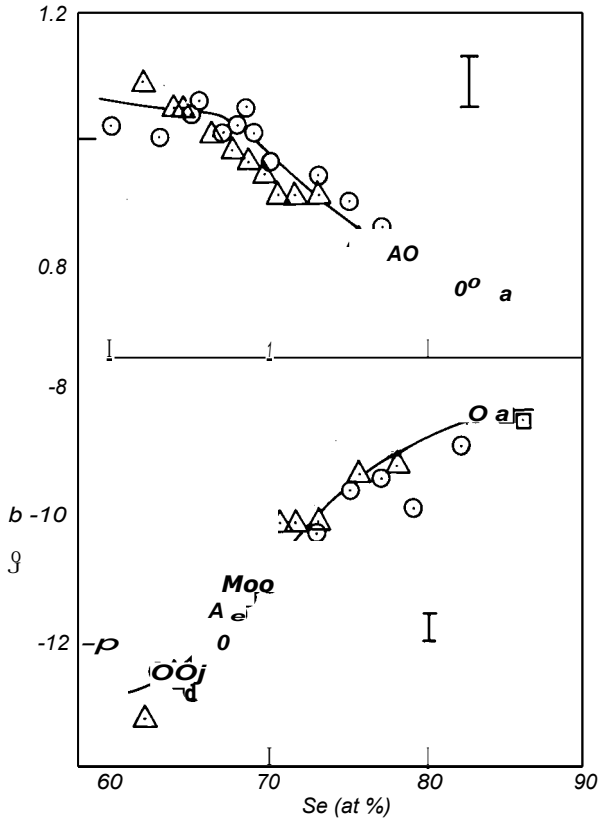


*Figure 5* Variation of (a) $AE$ and (b) log a (at 360 K) with selenium content for the (0) $Ge.1n_5Se_{95-s}$ and *(A)* $Ge.1n_8Se_{92}$ glasses. (0) Data for compositions 1 and 2 of Table I. The vertical bars denote the scatter in $AE$ and a.

states in these materials - those which pin the Fermi level and those which result in a shift or the unpinning of the Fermi level [14-25].

Understanding of some experimental observations based on the formation of charged defects, namely, the valence alternation pairs (VAP) and the intimate valence alternation pairs (IVAP), is well established in chalcogenide glasses [16-23]. In chalcogenides, the formation of charged defects according to

$$2C02 \qquad C3 + C1 \qquad (1)$$

is favoured; as in the usual notation, the subscript denotes the coordination and the superscript the charge state. The concentration of the charged defects, $N_0$, as the chalcogenide melt is quenched to equilibrium at $T_g$, is given by [18, 19]

$$N_0 = n_0 \exp(-E_{vAP}/2kT_g) \qquad (2)$$

where $E_{vAP}$ is the energy needed to create a VAP (typically - 0.8 eV) and $n_0$ is the concentration of the chalcogen. The energy to create the VAPs may be reduced if the charged defects form close to each other because of the coulomb energy of attraction, resulting in the formation of the so-called IVAPs [22]. While the VAPs pin the Fermi level, the IVAPs do not [22, 26].

The addition of certain elements such as silver, copper, zinc, indium, etc., which have less than four outer shell electrons, to chalcogenide glass melts can form four-fold coordinated negative charges [4, 19, 20]. In the Ge-In-Se system under investigation here, addition of indium to Ge-Se results in the formation of negatively charged $In_4$ from the neutral $In_3$ state according to

$$In^{\circ} + C^{\sim} \longrightarrow In4 + C^{0} \qquad (3)$$

which, with Equation 1 gives

$$In^{\circ} + C^{\circ} \longrightarrow In4C3 \qquad (4)$$

The observed changes in the $AE$ and 6 of the Ge-In-Se glasses indicate that the Fermi level is unpinned in these glasses. This unpinning of the Fermi level indicates that the corresponding correlation energy for the interconversion of the charged defects has a positive value [ 18, 20, 22, 25] due to the presence of IVAP on the introduction of indium [20]. A positive correlation energy is indeed to be expected based on the increase in ionicity on introduction of indium, and also due to the presence of chemical ordering in chalcogenide glasses [20]. Further, from trap-limited conductivity and ionicity, a positive value for the correlation energy has been inferred for $GeSe_2$ glass [18, 20].

For the composition $Ge_{12}In_5Se_{83}$ (chosen as the reference composition for the family with 5 at % In), $AE$ is seen to be approximately two-thirds of $AE$ of the corresponding Ge-Se glass. A reduction of this magnitude is possible according to the charged dangling bonds model [21] under the condition that $p = (2N_a/[A^-])$ where, with the usual notation [19, 21, 24, 27] p is the concentration of holes, $N_a$ is the concentration of charged defects and $[A^-]$ is the concentration of charged "dopants" or additives, and p is given as

$$p = [A^-]N_a \exp(E_F - E_v/kT)/2N_o \qquad (5)$$

For the $Ge_{12}In_5Se_{83}$ glass, which has a density of 4.48 $gcm^{-3}$ [2], $[A^-]$ is equal to 2.24 x $10^{21}$ $cm^{-3}$; this composition has $T_g$ = 372 K (Table I). Using the standard value of $n_o$ $10^{22}$ $cm^{-3}$, the concentration of charged defect centres, $N_o$ (using Equation 2) = 3.78 x $10^{16}$ $cm^{-3}$. These factors give a value of 1.3 x $10^{12}$ for $2N_o/[A^-]$.

Using a value of 0.87 eV for the $(E_F - E_v)$ at 360 K of the corresponding undoped Ge-Se glass (after taking note of a reduction of about 0.2 eV in the band gap with temperature via $(E_F - E_v) = AE - yT$, where $AE$ is 1.07 eV and y is typically 6 x $10^{-4}$ eV $K^{-1}$ [27]) and the typical value of $10^{20}$ $cm^{-3}$ for $N_v$, the value of p, as estimated from Equation 5, is 2.7 x $10^{12}$, in agreement with the factor 2 $N2/[A^-]$ evaluated above. Compositions 1-4 (Table I, Fig. 5a) which have a density, $T_g$ and indium content close to that of the reference composition, also show a reduction in $AE$ by about one-third of the value from those of the undoped Ge-Se glasses.

Fig. 6b depicts schematically the shift of the Fermi level which occurs in the $Ge_{12}In_5Se_{83}$ reference composition compared to that in the undoped Ge-Se glass (Fig. 6a). The defect states can either be doubly occupied (C1 state) or unoccupied (C3 state), while the neutral $C_2$ centres are singly occupied [22, 23]. For the case of the positive correlation energy under consideration here, the levels of the singly occupied C02

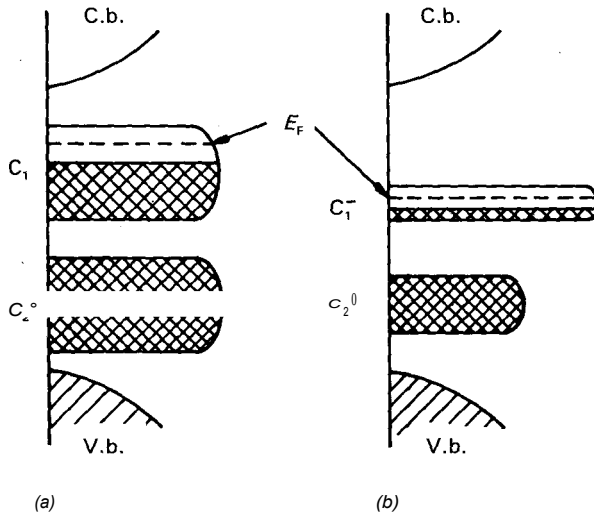


*Figure 6* Schematic drawing showing $E_F$ and levels of the charged centres for the case of positive correlation energy for (a) Ge-Se glasses and (b) Ge-Se glasses with indium as a modifier.

centres lie below those of the doubly occupied C1 centres, while those of the unoccupied C3 states are located above the C, state [22]. In the undoped material (Fig. 6a), the Fermi level is shown to be located midway between the highest occupied and the lowest unoccupied level. Formation of $In^-$ centres on the introduction of indium is achieved by reducing the concentration of the acceptor-like Ci centres. This leads to a shift of the Fermi level towards the valence band (Fig. 6b), thereby reducing 4E.

For the $Ge_xIn_5Se_{95-x}$ family, an increase in AE is seen (Fig. 5a) with decreasing selenium content. With decreasing selenium content, which results in an increase of $T_g$ (Table I), the concentration of the C, and C3 centres can be expected to increase as the corresponding melts equilibriate at higher $T_5$. However, because the concentration of indium is the same across the compositions of the $Ge_xIn_5Se_{95-X}$ family, the concentration of the C1 centres that are neutralized by the indium atoms is unaltered. There is thus a net increase in the concentration of unneutralized C1 centres with decreasing selenium content in the various compositions. This results in a shift of the Fermi level away from the valence band corresponding to its position in the reference composition (Fig. 6b) leading, as observed, to the increase in AE with decreasing selenium content. For selenium contents lower than 70 at %, the concentration of charged centres is larger (by about two orders of magnitude due to the higher $T_g$ of 550 K) compared to that in the reference composition. At this stage, indium no longer plays the role of an additive and an essentially constant AE results for the compositions.

The discussions are similar for the GexIn8Se92 $_{-x}$ glasses whose AE and a variation with selenium content are similar to those of the glasses of the $Ge_xIn_5Se_{95-x}$ family. The role of indium as an additive in affecting the AE and a values is found to saturate at about 2 at % In in the $Ge_{20}Se_{80}$ glass [4]. The agreement in the AE and a values of the glasses of the families with 5 and 8 at % In (Fig. 5a and b) can be traced to this saturation effect.

The tie-line compositions have a 4E of 1.14 eV, which is the same, to within experimental error, as those of the undoped Ge-Se glasses. These compositions (with - 65 at % Se) are all equilibriated at temperatures higher than 600 K and have such a large concentration of charged dangling bonds that indium no longer plays the role of an additive; these compositions must be treated as regular three-component glasses.

It is interesting to note that changes in slope in the 4E versus composition data (Fig. 5a) occur at compositions $Ge_{13}In_5Se_{82}$ and $Ge_{26}In_5Se_{69}$ which have [2, 3] Z values of 2.41 and 2.67, respectively. These Z values correspond to the two topological thresholds associated with the floppy to rigid transition [28-31] and the structural transition [32] occurring in network glasses; in the v-Z, where v is the mean atomic volume, and $T_g$-Z data of these glasses also, features were observed [2, 3] at Z - 2.40 and 2.67 corresponding to these two topological transitions. A change in slope in the optical band gap energy (which is twice the activation energy for d.c. conductivity in many chalcogenide glasses [33]) versus Z at Z 2.40 is seen for the Ge-Se and As-S systems [32]. From the data available for a limited number of systems, namely Ge-Se and Ge-S systems [32], a peak in the optical band gap energy is observed at Z 2.67 [32], but the present data indicate only a change in slope in AE versus Z data at Z - 2.67.

### 4.2. Temperature dependence of cr

The mechanisms for d.c. conductivity in amorphous semiconductors have been discussed at length in the literature [11, 34-38]. Four mechanisms, listed below, are proposed for the observed conduction. They are due to (a) carriers excited into the extended states beyond the respective mobility shoulders, also called the band conduction, which is generally operative at high temperatures; (b) carriers excited into the localized states at the band edges, also called thermally assisted tunnelling and observed at intermediate temperatures; (c) carriers hopping between localized states near the Fermi level, $E_F$, generally operative at low temperatures; and (d) small polaron hopping within a "dominant constituent", with associated hopping energy, which can be operative over the entire range of temperatures.

With the exception of mechanism (c) which results in a linear log a versus $T^{-1}$"' dependence, all the others indicate a variation of (7 with temperature of the form a = C exp ( - *AE/2kT).* The constants C and AE vary for the four mechanisms, with $C_a$ $C_b > C_c$; $C_a$ – $C_d$ and $AE_a > tE_b > tE_c$; $tE_a$ $IE_d$. The usual range for $C_a$ is from $10^2$-10' $52^{-1}$ $cm^{-1}$. C, is generally less than $C_a$ by a factor of $10^3$-10', and C. is even lower than $C_b$. Usually, owing to the high density of defect states, (b) will not dominate in any temperature range and a direct transition from (a) to (c) will result when the temperature is lowered [11].

From the values of C and AE observed for the Ge-In-Se glasses, it is possible to identify either the mechanism (a) or (d) over most of the temperature range for various compositions (Figs 1-4). This is

because the mechanism of small polarons hopping within a "dominant constituent", also gives C and $AE$ values which are similar in magnitude to those of the band type of conductivity [11]. Thermoelectric power measurements on these glasses are required to ascertain [11] whether mechanism (a) or (d) is operative in these glasses over most of the temperature range investigated. Around room temperature (between 300 and 330 K or 360 K) the slope of the log a versus 1/T data shows a decrease (Figs 1-3) for a few compositions. This is probably due to the setting in of the conductivity among localized defect states below around room temperature for these compositions.

## 5. Conclusion

The variation of a and $AE$ with composition and temperature is reported and discussed for $Ge_xIn_5Se_{95-x}$ and $GexIn\$Se92\_x$ glasses and also for glasses along the $GeSe_2$-$In_2Se_3$ tieline.

The addition of indium to Ge-Se glasses results in a decrease of $AE$ and an increase of a for compositions which have a selenium content higher than f-- 70 at %. The variation of $AE$ and a with selenium content is found to be similar for the families with 5 and 8 at In. A decrease of $AE$ with increasing selenium content in the glasses is seen for these families of glasses. These features have been traced to the conduction modulated by charged defects in these chalcogenide glasses. Changes in the concentration of charged defects brought about by the introduction of indium, which result in a corresponding shift of the Fermi level relative to the valence band edge are found to account qualitatively for the observed composition dependence of $AE$ and a of the Ge-In-Se glasses.

The log a versus 1/T data of these glasses is linear with a single $AE$ for the glasses over most of the temperature range investigated. The conduction is either due to the transport of carriers in the extended states, or due to the formation of small polarons. Over a narrow region around room temperature, the slope of the log a versus 1/T data decreases for many compositions. This is probably due to the setting in of the conductivity among localized defect states for temperatures below around room temperature.

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